1

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PHOTOGRAPHIC PROCESSES AND ELEMENTS Roger Gaston Louis Audran, Jean-Claude Hilaire, and Jean Alexandre Louis Bourdon, Paris, and André François Pierre Lestienne, Bordeaux, France, assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey No Drawing. Filed May 3, 1967, Ser. No. 637,047 Int. Cl. G03c 1/72

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19 Claims

ABSTRACT OF THE DISCLOSURE

The ability of an enzyme to hydrolyze protein can be altered upon exposure to light in the presence of a photosensitive material, thus permitting the production of photographic images. The enzyme can be converted from an active state to an inactive state, or vice versa. After exposure, development with water hydrolyzes and removes the protein from those areas where the enzyme is 20 which catalyzes the conversion of the enzyme to an inpresent in the active state.

This invention relates to novel photographic processes and to photosensitive compositions and elements for use 25 in such processes. In a particular aspect it relates to a photographic process in which the ability of an enzyme to hydrolyze gelatin is employed in the production of an

Methods for the preparation of photographic images 30 using silver compounds are well known. However, because of the cost and relative scarcity of silver, there is a constant search for photosensitive systems which will reduce the dependence of the photographic industry on this ods based on compounds other than silver have been developed. Examples of such other methods include xerographic processes, electrophotographic processes, diazo processes, processes employing photopolymerization and photocrosslinking, etc. None of these systems, however, 40 have been applied in as broad a range of uses as have the various silver systems. Furthermore, many of them have various processing or handling limitations which restrict or complicate their use. Such limitations include, sensitivity to only specific types of radiation, impermanence 45 of the image produced, complicated equipment necessary to produce an image, numerous and complicated processing steps, etc. Thus the search for new photographic systems continues in order to avoid the limitations of prior art systems and to further reduce dependence upon silver 50 compounds. systems.

It is an object of the present invention to provide novel photographic processes.

It is a further object of this invention to provide novel photographic processes which require a minimum of 55

It is still a further object of this invention to provide novel photographic processes in which an image can be developed by simple processing steps.

It is another object of this invention to provide novel 60 photosensitive compositions and elements for use in these processes.

These and other objects will be apparent to those skilled in the art upon studying the more detailed description of this invention which follows.

The compositions and processes of the present invention provide a useful method for the production of photographic images which is different from previously known processes. This process makes use of the ability of enzymes to attack and hydrolyze proteins, thereby breaking 70 down the protein into smaller molecules which are readily soluble in water. It has now been found that this

2

ability of enzymes to hydrolyze protein can be used in photographic systems by employing light sensitive materials which are capable of altering the activity with which enzymes hydrolyze protein. Thus, according to the present invention there is provided a composition comprising a protein, an enzyme or enzymes which can exist in an active state in which they hydrolyze protein and in an inactive state in which they do not hydrolyze protein, and a photosensitive material or a group of photosensitive 10 materials which in the presence of light convert the enzyme from one state to the other. On exposing this composition to light, the ability of the enzyme to hydrolyze the protein is altered, thus permitting one to establish a differentiation between exposed areas and non-exposed 15 areas.

In one embodiment of the present invention an enzyme is present in its active state in which it is capable of hydrolyzing protein. In this embodiment, exposure to light converts the photosensitive material to a material active state in which it is not capable of hydrolyzing protein. Thus, in this embodiment, the protein in exposed areas is not hydrolyzed and remains intact while in unexposed areas it is hydrolyzed and may be removed easily.

In a second embodiment an enzyme is initially present in an inactive state in which it is not able to hydrolyze and degrade protein. On exposure to light the photosensitive material converts the enzyme to an active form in which it is capable of hydrolyzing protein. Thus, in this embodiment, the protein is hydrolyzed and can be removed from exposed areas, while in unexposed areas the protein remains intact.

A wide variety of proteins can be employed in the pracmetal. Thus over a period of time, photographic meth- 35 tice of the present invention. Such proteins include globulin, glutin, casein, keratin, etc. However, the preferred protein is gelatin, because of its availability, its transparency as well as its hydrophilic and film-forming char-

> The enzymes which are particularly useful in the practice of the present invention are the protease enzymes such as trypsin, papain, erepsin, pepsin, chymotrypsin, bromelin, rennin, etc., and various other bacterial proteases and fungus proteases. In their active form these enzymes actively hydrolyze proteins such as those mentioned above in the presence of water. However, these enzymes become inactive and can no longer hydrolyze protein when they are oxidized or when they are blocked, for example, by complexing or chelating them with other

> The photosensitive materials that are used advantageously according to the present invention comprise a great number of compounds known up to now for playing the role of photosensitizers in photooxidation reactions. It seems that in the reactions of the present invention they play a different role, or different roles depending upon the embodiment in which they are used. However, the essential point is that under the action of light and in the presence of these photosensitive materials, the enzyme is converted to the desired form. Included among the photosensitive materials which are useful in the practice of the present invention are dyes such as fluorescein and its derivatives, such as rose bengal, erythrosin, eosin, etc., riboflavin, various thiazinic compounds, such as methylene blue, thionine, etc., derivatives of acridine, such as proflavine, acriflavine, etc. Particularly useful are photoreducible dyes according to the definition given by G. Oster which is described in the article by J. Spikes and B. Glad, in Photochem. and Photobiol. Journal 3, (1964) p. 479.

> In a preferred embodiment of this invention in which the enzyme is present in its active state, there is provided a composition comprising gelatin, an enzyme, a photo-